

# NATIONAL BUREAU OF STANDARDS REPORT

8690

QUARTERLY STATUS REPORT FOR THE QUARTER ENDING 4/30/65

ON

THE MECHANISM OF STRESS CORROSION OF TITANIUM ALLOYS  
EXPOSED TO SODIUM CHLORIDE AT ELEVATED TEMPERATURES

by

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for

Headquarters

National Aeronautics and Space Administration

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**U. S. DEPARTMENT OF COMMERCE**  
**NATIONAL BUREAU OF STANDARDS**

THE MECHANISM OF STRESS CORROSION OF TITANIUM ALLOYS  
EXPOSED TO SODIUM CHLORIDE AT ELEVATED TEMPERATURES

Work has continued with the use of hollow specimens of the Ti-8Al-1Mo-1V alloy described earlier. The specimen is heated externally with a heating tape, filled with a 10% aqueous solution of NaCl or of 7 parts NaCl + 1 part  $MgCl_2$ , and the solution slowly pipetted out. This leaves a layer of crystals (not necessarily uniformly) on the inner surface of the specimen. The specimen is closed with a plug of the Ti-8-1-1 alloy which has a 1/8 inch O.D. nickel tube extending through it so that the specimen cavity can be evacuated or a desired atmosphere introduced. The specimen is placed in a conventional creep furnace and is stressed using a modified creep apparatus.

Specimens are being heated to 750°F prior to stressing and are stressed (at temperature) to 90 percent of the yield strength at that temperature, i.e., 73,500 lb/in<sup>2</sup>. A gas sampling tube may be connected to the specimen cavity, through the nickel tube mentioned above, so that gaseous corrosion products can be withdrawn for mass spectrographic analysis.

The amount of applied salt on the specimen interior which has ranged in weight from 2.5 to 17 mg may influence specimen life statistically but shows no consistent relationship. Varying pressures of gaseous oxygen which have ranged from 150  $\mu$  to 10 psi do not effect

corresponding variations in specimen life. The most severe corrodent, giving the shortest specimen lives, has been the mixed NaCl -  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  crystals described above in combination with a dry oxygen atmosphere which, of course, offers a critical amount of water vapor on heating. With a small amount of excess water added to this system, specimen lives increased significantly. On the other hand, preliminary data on the pure NaCl corrodent indicate that moist oxygen gives more rapid attack than dry, although the range of the extremes of specimen life is smaller than that for the case of the mixed salt.

Experiments are presently being conducted to study effects in the absence of gaseous oxygen. Argon, purified through titanium turnings in a furnace tube and cold trapped, is placed in the evacuated specimen cavity at either atmospheric pressure or some nominal value (5 psi) above it so that a crack penetrating through the specimen wall will release the pressure and thus activate a switch in an elapsed time meter circuit so that the exposure period to failure is known.

Specimens are being studied that were coated with NaCl, NaCl +  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and NaCl +  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  + NaOH. Some specimens have also been heated in oxygen prior to coating with the corrodents in order to determine, if possible, whether a reaction can occur between the solid NaCl and titanium oxide that can lead to stress-corrosion cracking in the inner wall of the specimen.

A specimen that was preoxidized and coated with NaCl failed after 170 hours under stress at 750°F. This specimen was not baked while under vacuum and air could of course have been occluded on the walls.

One specimen containing NaCl,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , NaOH and filled with argon was free of macroscopic cracks, on examination, after 200 hours exposure. An examination for microscopic cracks has not yet been completed.

There are insufficient data at this time on which to base definite conclusions as to the importance of gaseous oxygen or the presence of NaOH in the system.

A group of sheet specimens of the mill annealed Ti-8-1-1 alloy were stressed at 40 to 80 percent of their yield strength as bent beams by four point loading. They were exposed in a circulating air furnace at 800°F until failures occurred. Exposure periods to failure generally increased with decreasing stress and ranged from 64 days for specimens stressed to 80 percent to 91 days for specimens stressed to 40 percent of their yield strength.

Two of the failed specimens are shown in Fig. 1. A crack extending across the specimen from one edge is shown in Fig. 2. This also illustrates the variety of corrosion products found on the specimen surface. A short length of crack is shown at much higher magnification in Fig. 3.

X-ray diffraction patterns were made of the corrosion products formed on these specimens. They indicated the presence of at least four phases, anatase, rutile, NaCl and at least one unidentified phase, designated X. The lines of the x-ray diffraction pattern of this phase are given in Table 1; lines marked by A or NaCl in the remarks column indicate that they may be a part of the pattern but there is an overlap with lines of anatase or NaCl.

A pattern obtained of the uncoated (under) side of the specimen indicated that NaCl and the unknown phase X were present. Some NaCl had apparently crept around the specimen after it had been coated.

Efforts were made to separate the corrosion products shown in Figs. 2 and 3 as to color and other physical characteristics. The white translucent material, Fig. 2, contained some NaCl and larger amounts of anatase, rutile and the unknown phase X. Three other corrosion products clearly distinguishable on the original specimens but difficult to differentiate in a black and white photograph were also studied. These all contained NaCl, anatase, rutile and the unknown phase. They differed, however, in the relative amounts of these different materials.

It was not possible by mechanical means to obtain any of these products completely free from all other products. A satisfactory pattern of the material in the crack and pits has not been obtained.

Surfaces that were not coated with NaCl did not develop anatase or rutile layers thick enough to be identified by x-ray diffraction techniques.

A re-examination of an x-ray diffraction pattern obtained earlier from material on the inner wall of one of the failed hollow specimens that had been coated with NaCl showed a trace of the X-phase in addition to anatase and NaCl.

Patterns of anatase and rutile indicated a pronounced preferred orientation of these oxides. The habit plane for rutile was the (110) and for anatase the (101).

X-ray diffraction patterns were also obtained at temperatures on the surfaces of specimens coated with  $\text{NaCl} + \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  stressed and heated to various temperatures. The jig for holding and stressing the specimens is shown in Fig. 4. The jig and specimen in place in the x-ray machine in Fig. 5 and the surface of a specimen, after it had been cooled to room temperature, in Fig. 6.

In order to determine what function the  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  may have in the corrosive process one specimen was coated with a one to one mixture of NaCl and  $\text{MgCl}_2$  and heated slowly to 1180°F. At 190°F the  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  was rapidly converted to  $\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ . This was stable to 260°F at which temperature it again lost water of crystallization and at 385°F it had changed to  $\text{MgCl}_2 \cdot 2\text{H}_2\text{O}$ . Above 385°F this phase

decomposed to an amorphous or glassy structure which persisted to about 680°F. At 680°F the glassy phase gradually disappeared and MgO slowly appeared. At 910°F the principal line of the pattern for rutile appeared only to disappear as the temperature was raised and reappear when the temperature was held constant until 1180°F was reached. At that temperature the pattern for rutile became definite and was retained upon heating to higher temperatures and after cooling to room temperature.

The x-ray patterns obtained on specimens coated with the 7 parts NaCl + 1 part  $\text{MgCl}_2$  solution and heated to 900°F never showed a MgO phase. This would indicate that the  $\text{MgCl}_2 \cdot x\text{H}_2\text{O}$  was never completely decomposed to MgO. Upon cooling there were patterns for rutile and NaCl. There was no change in the NaCl lattice spacing after the mixture had been heated and then cooled to room temperature. This indicated that there was no solid solution of another material in the NaCl at room temperature.



TABLE 1. DIFFRACTION PATTERN FOR "X" PHASE.\*

<u>d-spacing</u>	<u>I**</u>	<u>Remarks</u>
4.88	< 5	?
3.91	35	
3.76	35	
3.48	35	A***
3.23	10	NaCl
2.81	100	NaCl
2.63	60	
2.54	< 5	
2.37	35	A
1.992	40	NaCl
1.959	10	
1.882	< 5	A
1.742	30	
1.691	< 5	A
1.623	20	NaCl
1.581	< 5	
1.567	< 5	
1.458	< 5	
1.406	< 5	NaCl
1.263	10	NaCl
1.152	5	NaCl

\* Sample taken from washings allowed to dry on glass plate.

\*\* Relative intensities - visually estimated.

\*\*\* A stands for anatase ( $\text{TiO}_2$ ). The entries under remarks represents d-spacings which may be caused entirely or in part by the substance indicated. ? stands for a d-spacing found only in some patterns.

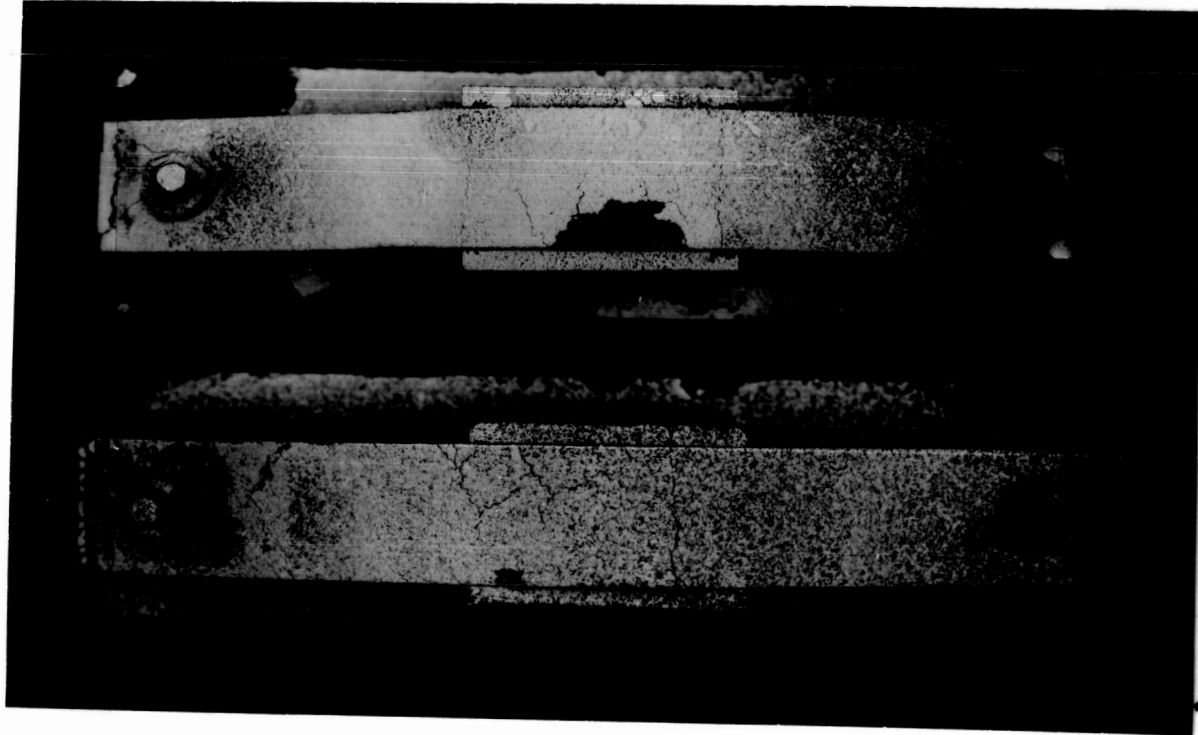


FIGURE 1. Sheet specimens stressed by four point loading, upper to 60,000 lb/in<sup>2</sup>, lower to 80,000 lb/in<sup>2</sup>. Failures occurred after approximately 64 days at 800°F. X 1

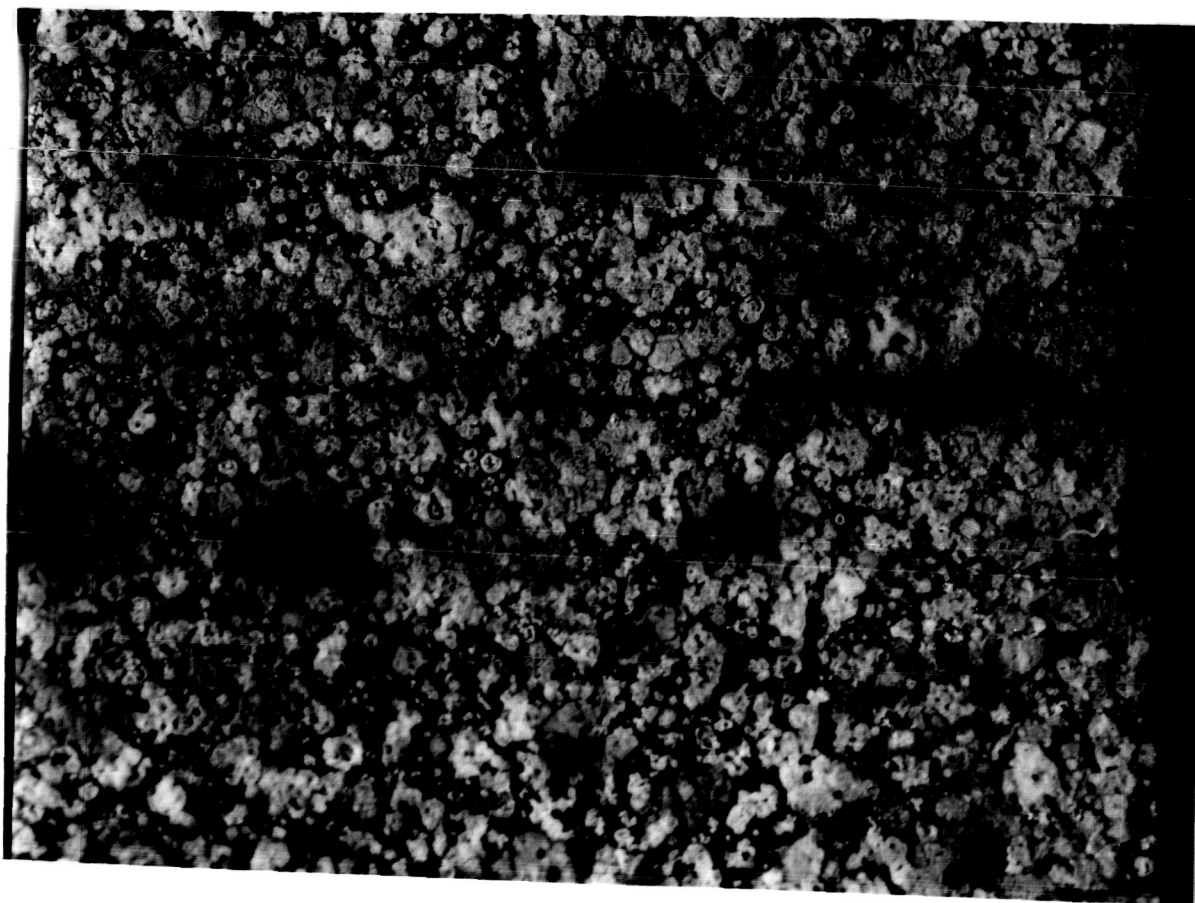


FIGURE 2. Cracks in specimen shown in Fig. 1. White translucent material contains NaCl and larger amounts of anatase, rutile and X phase. Light grey contains small amounts of NaCl and rutile and large amounts of anatase and X phase. The dark grey is primarily rutile. X 8

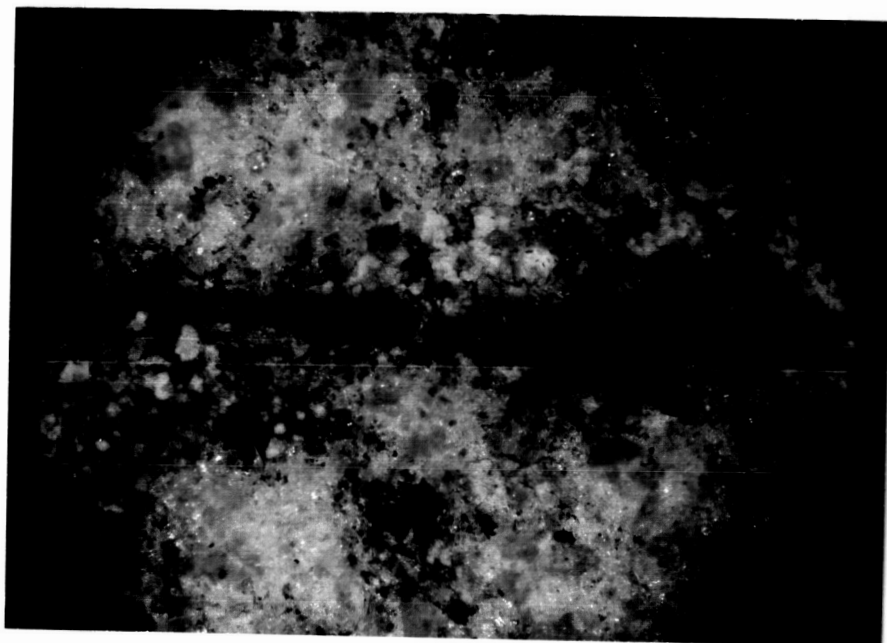


FIGURE 3. Part of crack and corrosion products shown in Fig. 2 at higher magnification. Polarized light. X 100

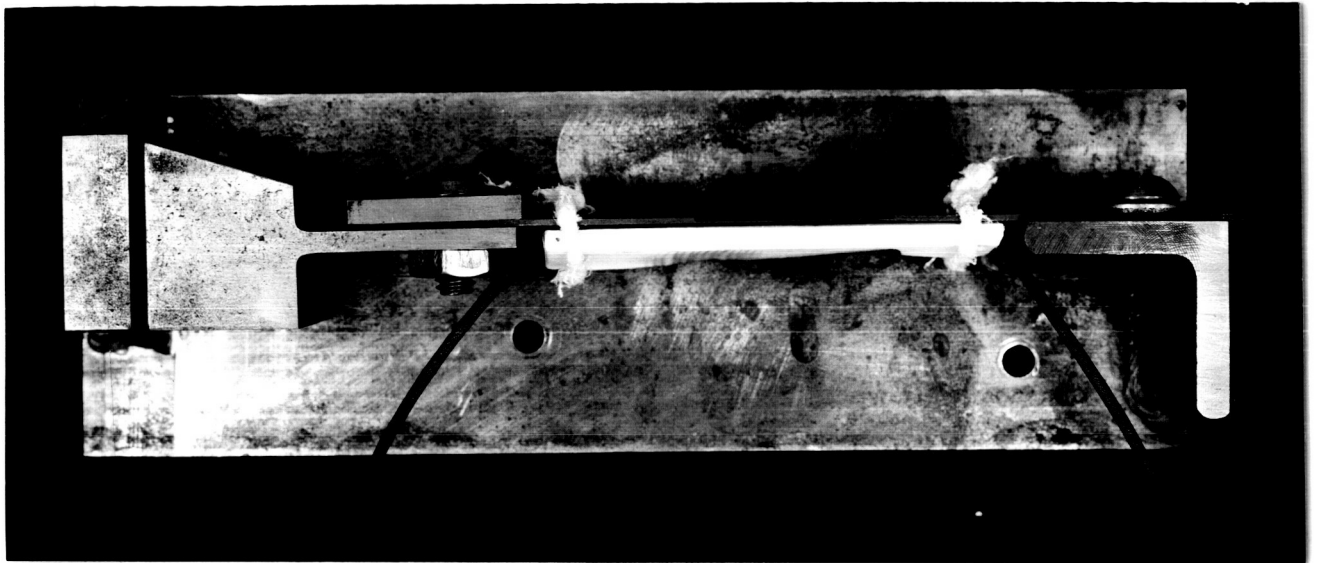


FIGURE 4. Side view of jig and specimen for x-ray diffraction studies at temperature. Specimens were heated electrically from the under side and were extended about 0.01 inch (i.e., 1% in the thin section).

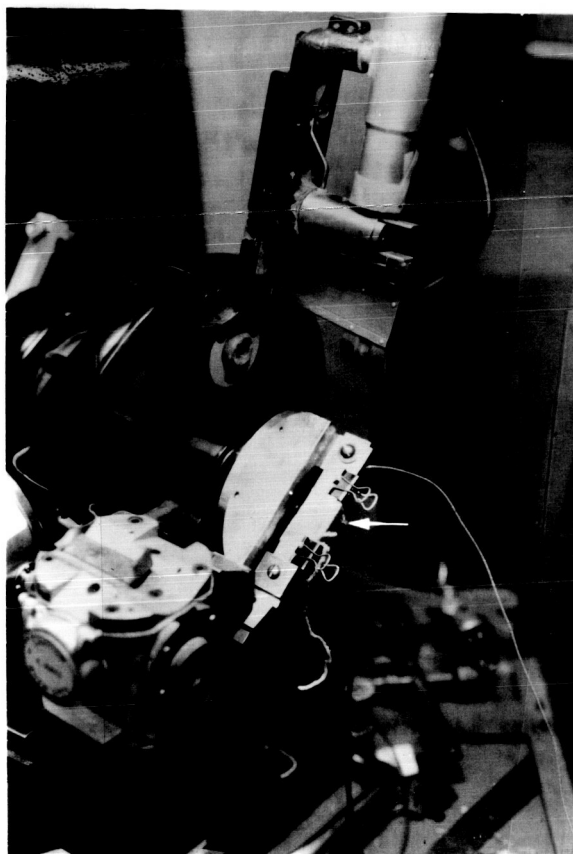


FIGURE 5. Specimen, marked by arrow, in place in x-ray machine.

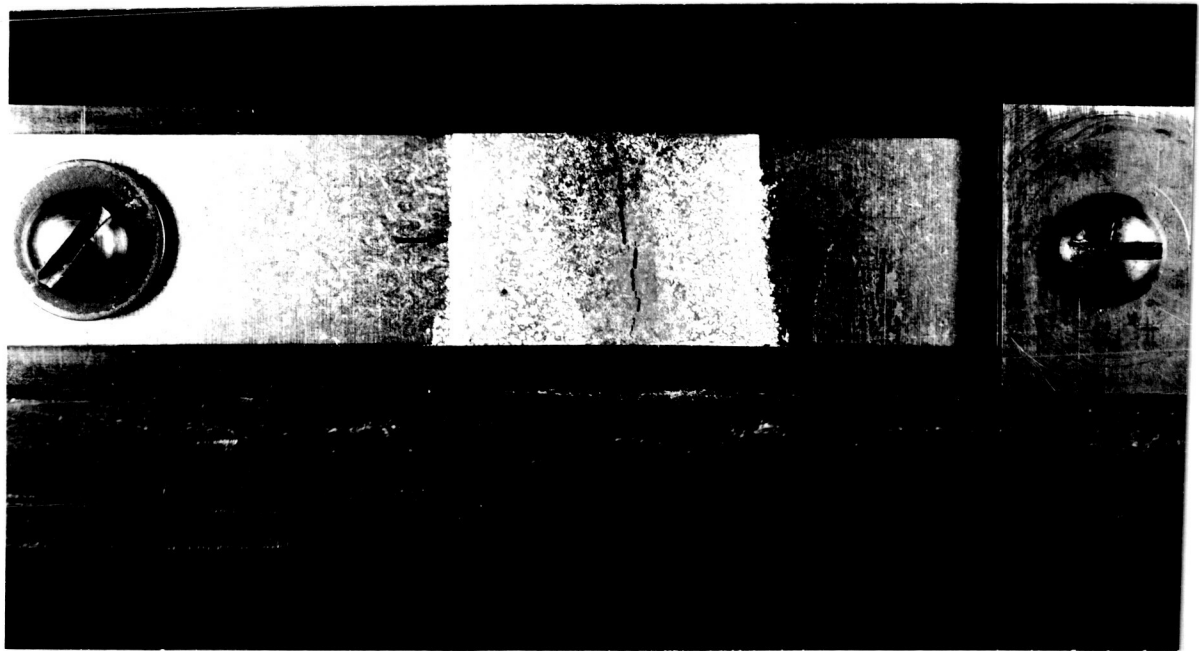


FIGURE 6. Top surface of specimen that had failed at temperature under stress in jig used in x-ray diffraction studies at temperature. Light colored area, between arrows, was heated and studied. X 1-1/4